SCIENCE FOR CERAMICS PRODUCTION

PARTICULARS OF THE TECHNOLOGY OF HIGH-DENSITY TECHNICAL CERAMICS. CRYSTAL GROWTH DURING SINTERING[1]

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Growth of the crystals which compose a ceramic is observed at the final stage of sintering or during use at high temperatures. This is due to surface tension forces (in the present case boundary tension) as a result of diffusion or cooperative mass transfer (shear; rotation).

The microstructure of oxide ceramic is determined by, aside from the conditions under which the intermediate product is obtained, the structure of the initial powder, the form and distribution of the modifying additive, and the annealing regime. As a result of the presence of defects it is always metastable and it undergoes substantial changes during use at high temperatures, a result of which is that many properties, first and foremost, the mechanical properties, change [1]. At the same time many varieties of ceramics are used under essentially normal conditions when mass transfer is a very slow process.

Internal boundaries separating crystals of the same phase or different phases are present in any polycrystalline body. In any case they comprise a region or zone of imperfect contact (disruption of continuity of the microstructure), i.e., sections with higher energy. Consequently, there exists a driving force that strives to decrease the surface of the boundaries and, correspondingly, cause them to move — the so-called "boundary tension" analogous to surface tension [2].

Ordinarily, it is assumed that the width of the disordered boundary region is close to atomic dimensions. In this case, the number of atoms with elevated energy in the "amorphized" intercrystalline interlayer is limited to a minimum. Depending on the angle of disorientation of the crystals, these regions can be described by a definite set of surface (planar) dislocations and vacancies [3]. A model according to which sections of good and poor matching of neighboring lattices exist on such boundaries has been proposed for large angles. In the first case, they can be constructed from dislocations and vacancies, and in the second they consist of amorphized matter. Twinning is a case of a small-angle boundary. The atoms lying in the twin plane are coherently bound with each adjoining crystal, the distances between these atoms and their nearest neighbors remain unchanged, and the mismatch in the arrangement exists only for the second-nearest and more distant neighbors. Examples of twins in a ceramic are the boundaries between crystals in optically transparent materials and between different phases in high-strength structural materials, for example, in the system $Al_2O_3 – ZrO_2 – Y_2O_3$. It should be noted that they are inherent to very stable microstructures.

The crystals increase in size at the final stage of sintering or during use of the ceramic at high temperatures [4]. The driving force of this process is the decrease in free energy when atoms pass through an interface from the convex to the concave side, where the atoms occupy equilibrium positions (lattice sites). According to the generally accepted picture, as a result of this the interface moves in the direction toward its center of curvature and large crystals grow at the expense of small ones. Ultimately, the total boundary area per unit volume decreases. In what follows we shall distinguish two processes which give rise to structural changes on heating — crystal growth and recrystallization. In the first process the crystals in a polycrystalline body grow as their boundaries move. The driving force is the boundary tension associated with the curvature and extent of the boundary. The second

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[1] We continue the publication of articles with a common theme (see the 2008 issues Nos. 2 – 4, 6, and 7).

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process is the formation and growth of crystals in a highly distorted matrix as a result of the presence of a large number of lattice defects of different kinds. The driving force of this process is the difference of the chemical potentials of the volume of the stressed medium and growing crystal with fewer defects, which proceeds by diffusion.

Thus, crystal growth in a polycrystalline material consists of geometric changes of the three-dimensional "network of boundaries" in the material; inclusions of another phase, including pores, impede the motion of the network [5]. The expression relating the change of the size of the crystal in time τ at constant temperature T has the form

$$D^2 - D_0^2 = K\tau,$$

where D and D_0 are the final and initial size of the crystals; K is the rate constant, which changes with temperature:

$$K = K_0 \exp[-Q/RT],$$

where K_0 is a pre-exponential factor, Q is the activation energy, and R is the universal gas constant.

For a process with sufficiently long duration $D_0 \ll D$ the expression for the kinetics has the form $D^2 = K\tau$, and the plots of $\log D$ versus $\log \tau$ will be straight lines with slope angle tangent 0.5. However, in practice, the slope ordinarily lies in the range $0.1 - 0.5$. There could be several reasons for this, first and foremost, the fact that the presence of foreign inclusions, such as pores and a second phase, often impedes growth.

When the boundary of a growing crystal encounters an obstacle, the boundary energy decreases in proportion to the transverse cross section of the obstacle and energy inflow is required in order to overcome the obstacle. When a large number of inclusions are present, the inflow of energy could be insufficient to support continual growth of crystals. It is assumed that crystal growth stops when the following condition is satisfied [5]:

$$D_m = d/f,$$

where D_m is the maximum size of the crystals, d is the average diameter, and f is the volume fraction of the inclusions.

Ordinarily, the pore size is about 0.1 times the average diameter of a crystal, so that growth can start at porosity $f = d/D = 0.1$. This is observed in practice. For example, intense growth of crystals starts with open porosity of about 10% in MgO, $4 - 5\%$ in Al_2O_3, and $3 - 4\%$ in Y_2O_3.

The study of the growth kinetics during sintering of ceramic materials shows that the process is quite adequately described by the equation

$$D = K\tau^n.$$

According to some results, the values obtained for the exponent n are mainly the same or close to 1/3. For example,

crystal growth during sintering of CaO-stabilized ZrO_2 can be described with $n = 1/4$ and for corundum ceramic $n = 1/2$ [6].

The activation energy of corundum crystal growth is 505 kJ/mole, which is essentially equal to the sintering activation energy (496 kJ/mole). The activation energy of self-diffusion in Al_2O_3 is $460 - 480$ kJ/mole, which indicates that the process occurs by a diffusion mechanism. It has been determined that the activation energy of MgO crystal growth is 260 kJ/mole, and the sintering activation energy calculated according to the shrinkage is $230 - 280$ kJ/mole. Close values of the activation energy of sintering and crystal growth are characteristic for other oxides.

At the final stage of sintering the number and size of the pores reach a definite minimum value, as a result of which crystal growth becomes possible. Ordinarily, the crystals entrap a quite large number of pores. The boundaries move more rapidly than the pores can grow via vacancies, and for this reason a portion of the vacancies remains in the volume of the material and is not removed even with long holding times. The drive to decrease the free surface energy leads, on the one hand, to coalescence (merging) of pores with their volume remaining unchanged (internal sintering) and, on the other, to closure, which is accompanied by an increase of the pycnometric density (external sintering). If the average distance between the boundaries is much greater than the distance between the pores, regions where coalescence occurs predominantly can coexist with regions where pores close, dissolving via vacancies in boundaries-sinks. According to the diffusion theory of coalescence [7], the average pore size R in an isothermal process grows in time according to the relation $R \sim \tau^{1/3}$. The critical size above which they increase in size is 10^{-5} cm for oxide materials at 2000 K [8].

The microstructure of oxide ceramic materials intended for use at high temperatures must be stable during long-time heating to avoid changes in the properties, first and foremost, strength. We shall examine the growth of crystals during sintering and thermal aging for the example of periclase ceramic. We note that during thermal aging wide ranges of temperature and holding times are more favorable for investigations. They make it possible to establish a number of important features, which are characteristic also for sintering, i.e., with continual heating and then holding, of a porous compact. Phenomenologically, crystal growth occurs during the holding time, and is especially intense initially, slowing down with time; a temperature increase sharply intensifies it. Aging is accompanied by a gradual decrease in the number and size of intercrystalline pores. At the same time, the total volume of intracrystalline pores essentially does not decrease; it becomes larger and isometric, and the number of porous decreases [9].

Histograms were constructed to obtain the quantitative estimates of growth. These are differential and integral curves characterizing the size distribution of the crystals. An example of integral curves is presented in Fig. 1. It was
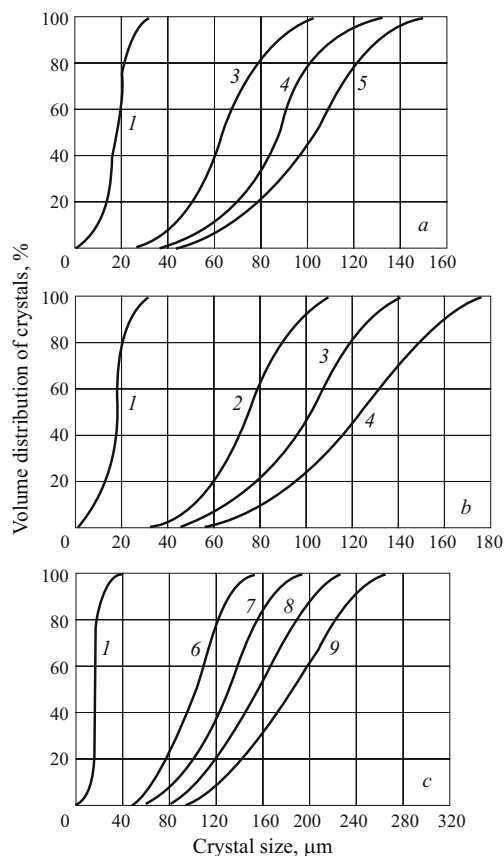
Fig. 1. Integral curves of the size distribution of crystals of periclase ceramic before (*1*) and after thermal aging at temperatures 1700°C (*a*) and 1900°C (*b*) for 2 h (*2*) 5 h (*3*), 10 h (*4*), and 20 h (*5*) as well as at temperatures 1800°C (*6*), 1900°C (*7*), 2000°C (*8*), and 2100°C (*9*) for 10 h (*c*).

Fig. 2. Microstructure of Y_2O_3 coarse-crystal transparent ceramic with the addition of 20% (molar content) Gd_2O_3 (× 115).

found that during the crystal growth process the relative uniformity of the ceramic structure remains unchanged in all cases; the conclusion is true for all types investigated: MgO, Al_2O_3, ZrO_2, $MgO \cdot Al_2O_3$, and others. This phenomenon can be very important technologically. According to our observations, the size distribution of crystals in a ceramic is determined by the particle-size distribution in the initial powder. To obtain uniform crystallization, whose relative dimensionality remains under all conditions of heating at high temperatures, it is necessary to use initial powders with the same particle size, preferably spherical particles. In this case, the pore sizes in the initial porous compact will be the same which will give uniform sintering over the volume of the part and makes it possible to obtain crystals with close sizes. The closer the distribution of the particles in the initial powder is to an ideal distribution (monofractional), the more uniform the structure of the ceramic and, naturally, the more stable the properties of the ceramic are.

As one can see from Fig. 1, not only the largest crystals but also the smallest crystals undergo growth. This contradicts the generally accepted law of growth — large crystals grow at the expense of small crystals, i.e., small crystals

should exist regardless of the size of the large crystals. In reality, small crystals are essentially absent in large-crystal materials (Fig. 2). It can be assumed that growth can also occur by means of other mechanisms.

Phenomenologically, the growth kinetics of periclase crystals, just as other oxides, is described by the equation $D = K\tau^n$. For fine-crystalline samples $n = 0.28 - 0.31$, and for coarse-crystalline samples n decreases to 0.18. It should be noted that substantial growth of crystals, which on heating to 1950 – 2100°C become larger than 400 μm, occurs in MgO ceramic. Impurities are displaced onto the boundaries of the crystallites, which results in the formation of interlayers of an intercrystalline phase.

The absolute instantaneous growth rate is inversely proportional to the square of crystal size and is described by the equation

$$\frac{dD}{d\tau} = \frac{A}{D^2}.$$

Introducing the kinetic law into this equation establishes the relative instantaneous rate as a function of time:

$$\frac{dD}{d\tau}\frac{1}{D} = A'\tau,$$

where A and A' are the coefficients of proportionality.

Crystal growth and microstructure changes greatly influence strength. As size increases, the strength initially increases somewhat and then decreases substantially (Fig. 3); the maximum crystal size is 90 – 100 μm. This increase is due to an increase in the density of the ceramic and removal of open porosity. Apparently, further decrease is due to an increase of thermal stresses on the boundaries of large disori-
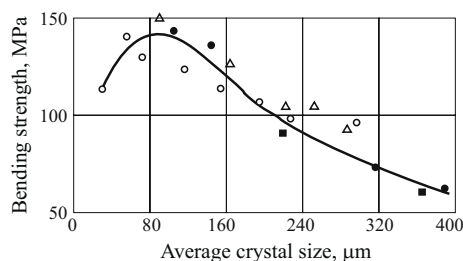
Fig. 3. Variation of the bending strength of MgO ceramic as a function of the average crystal size. The ceramic was heat-treated at 1700°C (○), 1800°C (△), 1950°C (●), and 2100°C (■).
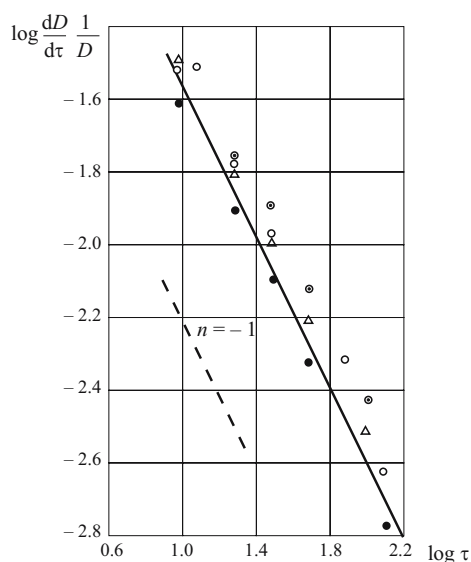

Fig. 4. Relative instantaneous growth rate of crystals of various oxide materials as a function of aging time: ○) Al_2O_3; ●) MgO; △) ZrO_2; ◉) $MgO \cdot Al_2O_3$.

ented crystals, arising during cooling, as a function of the aging temperature.

The behavior of ceramic with different composition and structure during long-time heating in a wide temperature range also has been studied in detail for aluminum oxide, zirconium dioxide, yttrium and scandium oxides, calcium oxi-

de, alumomagnesia spinel, and others. Similar behavior of the microstructure, crystal growth, and strength as a function of crystal size has been obtained. We note that the microstructure of ceramic consisting of yttrium and scandium oxides exhibits quite high stability, but the strength of these ceramics, just as those of other types of ceramics, decreases substantially. Samples of highly dispersed powder with a low degree of particle aggregation with no additives sinter at lower temperatures than the samples consisting of commercial powder, but they show crystal growth; crystal growth occurs at a lower rate than in ceramic on sintering.

Thus, a thermally stabile ceramic with density close to the theoretical value, set by the microstructure and high level of the properties, cannot be obtained in practice on the basis of pure oxides. High sintering temperatures and prolonged holding do not remove pores completely. In addition, the microstructures formed are unstable and can substantially reform during prolonged heating at high temperature, resulting in a change of the properties.

The growth of crystals of pure oxide materials during sintering and thermal aging is due to the motion of boundaries under surface tension, and the growth mechanism is diffusion. This is indicated by the fact that in most cases the activation energy for crystal growth is close to the activation energy for sintering (see Table 1).

The dependence of the relative instantaneous growth rate of crystals of pure oxide materials on the aging time (Fig. 4) shows that the type of oxide, the size of the crystals, the temperature, and the type of process (sintering or thermal aging) did not influence it; this quantity is inversely proportional to the holding time. Therefore, the experimental data show that during crystal growth the microstructure as a whole changes self-similarly and relatively uniformly.

Crystals grow, becoming at each moment in time larger by the same relative amount. It can be assumed that the growth mechanism is the same in all cases, and initially it is determined by motion of boundaries toward their center of curvature i.e., large crystals grow at the expense of smaller crystals. Apparently, this process is combined with diffusion reorientation of crystals, which reach a definite minimum size. The reorientation proceeds until neighboring lattices coincide geometrically, as a result of which the boundaries vanish (annihilation occurs) and large crystals unite with smaller crystals.

A small crystal in a comparatively coarse-crystalline matrix is a three-dimensional defect and, in this sense, behaves as a single whole. With adequate thermal activation it can turn and slip over small distances, i.e., adjust itself under a large neighboring crystal. This is especially true for initial powders which are obtained by chemical methods and have many defects. Such a growth mechanism explains the absence of small crystals and the shift of the initial branches of the distribution curves (see Fig. 1). Apparently, the larger the crystals in the overall mass, the larger the crystals that can be absorbed are. Examples of the vanishing of a boundary are shown in microstructures (Fig. 5).

TABLE 1.

Material	Activation energy, kJ/mole		
	sintering	crystal growth during sintering	crystal growth during aging
MgO	230 – 326[*]	260	293 – 347[*]
Al_2O_3	476 – 496[*]	502	343 – 420
ZrO_2	314	290	335
Y_2O_3	314	333	356

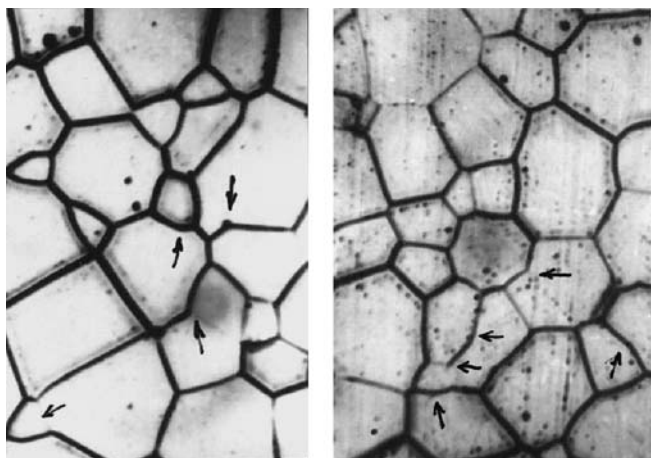[*] Data obtained by different authors.

Fig. 5. Microstructure of a transparent ceramic. Sites where boundaries vanish as result of possible reorientation of crystals are indicated ($\times$ 300).

Fig. 6. Scheme of coalescence of crystals, including a rotation stage: *a*) initial structure; *b*) moment of rotation of one crystals; *c*) structure immediately after coalescence; *d*) final structure of crystals and after some migration of the boundaries.

The merging of subcrystals as result of the reorientation of one of them has been observed in metals [10]. This phenomenon is shown schematically in Fig. 6. It is assumed that subcrystals can increase in size as a result of coalescence (merging), when boundaries of some neighboring subcrystals gradually vanish and at the same time the crystals merge, acquiring the same orientation. As a result of a process which includes climb, dislocations should gradually leave a vanishing sub-boundary, and the corresponding subcrystal should turn by a definite angle. The vanishing of the boundary *CH* (see Fig. 6) is accompanied by a rotation of one subcrystal as a result of the diffusion of atoms along sub-boundaries, as result of which material is transferred from the hatched regions into the corresponding unhatched regions.

Such a phenomenon can be clearly observed in a transparent ceramic. Figure 7 shows the microstructure of a transparent Y_2O_3 ceramic microsection with added Gd_2O_3 (crystal size $150 - 200$ μm). Judging from the remaining boundaries, the material consists of fine particles (about 10 μm), which have coalesced into large grains during sintering. This is confirmed by the ideas, advanced by the authors, on the possibility of crystal growth not only by diffusive mass transfer but also by shifting and rotation of amalgamations of atoms.

Introducing additives provides a real possibility for substantial change of microstructure (crystal size, porosity distribution, and pore size). Since the ionic radii of the main cation and the introduced cation are almost never the same, the lattice parameter changes, the sign of the change depending on the size ratio of the ions: if the additive is smaller, the lattice parameter decreases, otherwise it increases. Thus, the crystal lattice is in a stressed, distorted state, which has a large effect on the microstructure, microhardness, and strength of the ceramic as well as other properties.

As an example, Fig. 8 displays the change of the lattice parameter and crystal size of Y_2O_3 as a function of the type and concentration of the additive introduced, and Fig. 9
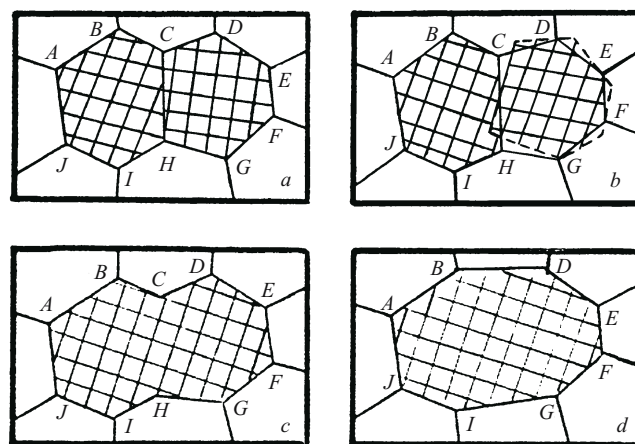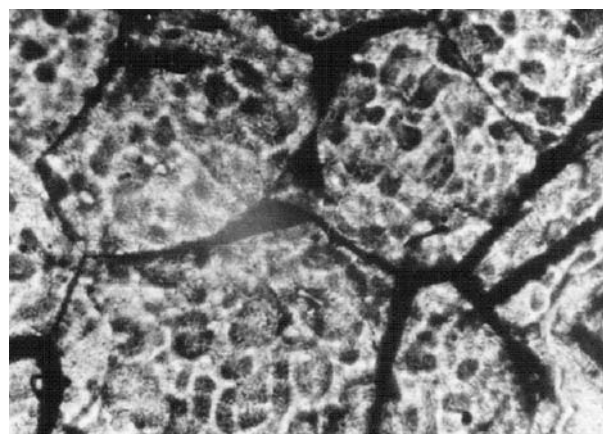

Fig. 7. Microstructure of a transparent ceramic based on Y_2O_3 with 20% (molar content) Gd_2O_3 added (transparent microsection, $\times$ 115).

shows the microstructure of a ceramic based on Y_2O_3 with HfO_2 and Gd_2O_3 added. Additives have a large effect on crystal size. This phenomenon is probably due to a change in the state of the atoms, including at a boundary. This is what either decreases or increases their transition energy.

Similar behavior is also characteristic for other oxides with a cubic crystal lattice. For example, when 40% (molar content) Y_2O_3 is added to Sc_2O_3 the lattice parameter increases from 0.985 to 1.015 nm, and the size of the crystals of the solid solution changes from 25 to 120 μm. Similar relations have also been established for the oxide compounds $3Y_2O_3 \cdot 5Al_2O_3$, $3Gd_2O_3 \cdot 5Ga_2O$, $MgO \cdot Al_2O_3$. Introducing into garnets $0.5 - 1.0$ wt.% ZrO_2 and HfO_2, which decrease their lattice parameter, produces a fine-crystalline structure in the ceramic.

In summary, when additives forming solid solutions are introduced into oxides and their compounds a completely
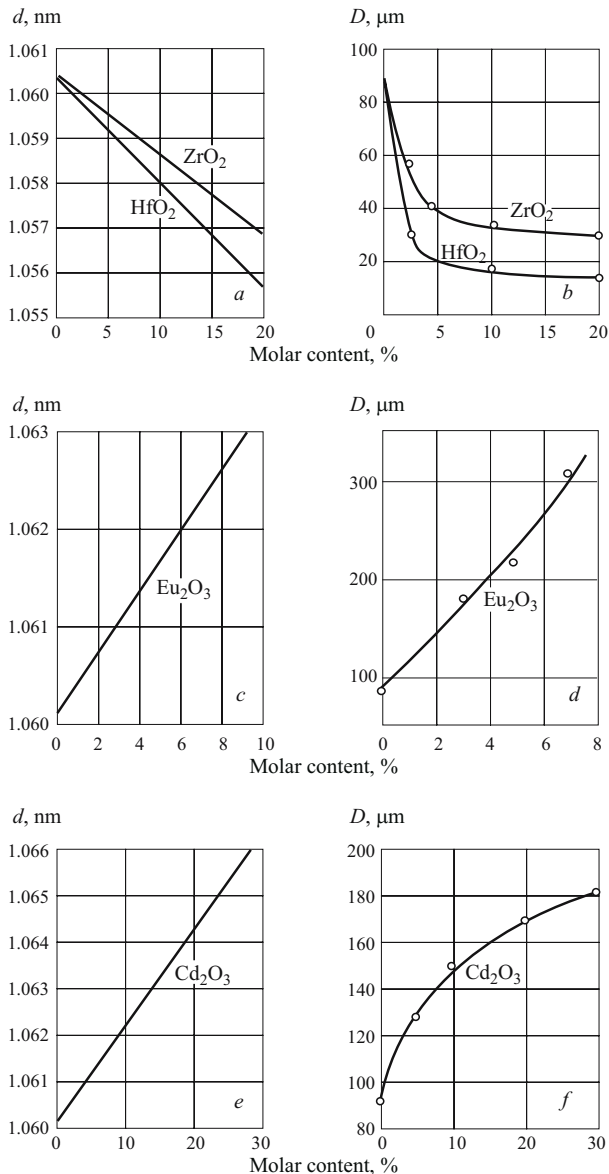
Figure 8 (left column graphs):

Fig. 8. Variation of the lattice parameter *d* and size *D* of Y$_2$O$_3$ crystals with the introduction of ZrO$_2$ and HfO$_2$ (*a*, *b*), Eu$_2$O$_3$ (*c*, *d*), and Gd$_2$O$_3$ (*e*, *f*).

Fig. 9. Microstructure of transparent ceramic consisting of Y$_2$O$_3$ (× 200) with added HfO$_2$ (*a*) and Gd$_2$O$_3$ (*b*).
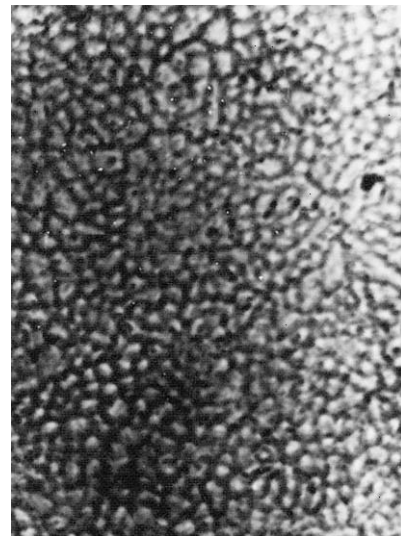
Fig. 10. Microstructure of transparent ceramic made from Y$_2$O$_3$ with Sc$_2$O$_3$ and HfO$_2$ added simultaneously (× 500).

definite crystallization is observed in all cases. This crystallization depends on the sign of the change of the crystal lattice parameter, which makes it possible to predict qualitatively the character of the microstructure of the new materials.

The simultaneous introduction of two oxides, one of which forms an isovalent solid substitution solution and the other a heterovalent solution, provides even greater possibilities for regulating the degree of sintering, microstructure, and properties. In this case, a substantial change of the lattice parameter can be attained, which makes it possible to obtain fine-crystalline materials with uniform microstructure. An example is the transparent ceramic based on Y$_2$O$_3$ with Sc$_2$O$_3$ and HfO$_2$ added simultaneously; the microstructure
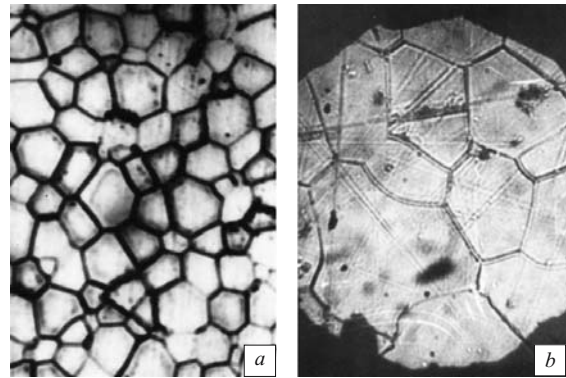
of the ceramic is shown in Fig. 10. The lattice parameter of the material decreases by 4% compared with the material with no additives. The strength of the composition 0.77Y$_2$O$_3$ · 0.2Sc$_2$O$_3$ · 0.03HfO$_2$ is three times greater than that of pure Y$_2$O$_3$ and approximately 2 times greater than that of the transparent ceramic with 5% HfO$_2$ added. This principle for obtaining a composition was used to obtain a transparent ceramic based on Sc$_2$O$_3$, ZrO$_2$, and MgO. The crystallization in this material is quite coarse, since the ionic radii of the additive cations are larger than the radius of the matrix cation.

At the present time, compositions where additives are used to regulate sintering, microstructure, and properties are widely used to make new structural materials. Combined with variations of the technology, this makes it possible to obtain highly dispersed non-aggregated powders which can be used to fabricate ceramic with a new structure, consisting not of the conventional faceted crystals but rather a dense

Fig. 11. Cleavage surface of a ceramic with the composition 70% Al_2O_3 and 30% ZrO_2 ($\times$ 10,000).

concretion of rounded particles and particles with a slightly elongated shape (Fig. 11).

We underscore once again that all laws of crystal growth which have been examined for materials with modifying additives forming solid solutions are valid only when the materials are made from highly dispersed powders with aggregates smaller than 1 μm and with uniform additive distribution over the volume of the particles.

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